Low-density limit of the correlation energy in the random-phase approximation for charged particles of arbitrary statistics

John P. Perdew
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

Hugh E. DeWitt
Lawrence Livermore National Laboratory, Livermore, California 94550
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Within the random-phase approximation (RPA) or ring sum, the ground-state correlation energy for a uniform gas of charged particles with density parameter r_s tends as $r_s \to \infty$ to $(-0.803\ \mathrm{Ry})\ r_s^{-3/4}$. This limit holds for fermions, as for bosons and distinguishable particles. For electrons, the next term in the low-density expansion (of order r_s^{-1}) cancels the exchange energy. Corrections to RPA must cancel the $r_s^{-3/4}$ term, and can modify the r_s^{-1} term.

The correlation energy of a many-body system incorporates all effects beyond the Hartree-Fock approximation. For charged particles with interaction $e^2/|\mathbf{r}'-\mathbf{r}|$, the random-phase approximation (RPA) for the correlation energy is of special interest, since its relative error vanishes in the high-density limit (at least for fermions).[1] Here we discuss the opposite limit of low-density or strong coupling, in which the weaknesses of the RPA should be most evident. We consider in particular the ground state of a uniform gas of density $\mathbf{n}$ with a neutralizing inert background, characterized by the density parameter

$$r_s = (3/4\pi n a_0^3)^{1/3}\ , \tag{1}$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius.

Recently, Wang and Perdew[2] showed that the $r_s \to \infty$ limit of the RPA correlation energy per particle for the electron (fermion) gas is

$$\varepsilon_c^{\mathrm{RPA}}(r_s,\zeta) = -d_0^{\mathrm{RPA}}(\zeta) r_s^{-3/4} + d_1^{\mathrm{RPA}}(\zeta) r_s^{-1} + \dots\ , \tag{2}$$

where $\zeta = (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$ is the relative spin polarization. From the Misawa spin-scaling relation,[3] which is exact within the RPA,

$$d_0^{\mathrm{RPA}}(1) = d_0(0)\ , \tag{3}$$

$$d_1^{\mathrm{RPA}}(1) = 2^{1/3} d_1(0)\ . \tag{4}$$

Rigorously, $d_0^{\mathrm{RPA}}(0)$ is positive,[2] not zero as had been expected. From a fit to numerical RPA correlation energies for r_s up to 10^6, Perdew and Wang[4] found $d_0^{\mathrm{RPA}}(0) = 0.80$ Ry and $d_1^{\mathrm{RPA}}(0) = 0.92$ Ry, where 1 Ry $= e^2/2a_0$.

Unbeknownst to Wang and Perdew, DeWitt[5] had analytically evaluated the ground-state RPA correlation energy for *distinguishable* charged particles, with the result $(-0.803\ \mathrm{Ry})\ r_s^{-3/4}$. He also argued that the RPA part of Foldy's calculation for charged bosons[6] gave the same result. Thus we assert that the low-density limit of the RPA correlation energy is independent of particle statistics. It follows that $d_0^{\mathrm{RPA}}(\zeta)$ for electrons is independent of ζ, consistent with Eq. (3).

The second term of Eq. (2) for the electron gas in the RPA evidently cancels the exchange energy, i.e.,

$$d_1^{\mathrm{RPA}}(\zeta) = (0.916\mathrm{Ry})[(1+\zeta)^{4/3} + (1-\zeta)^{4/3}]/2\ . \tag{5}$$

This assertion agrees with the Perdew-Wang fit[4] for $\zeta = 0$, and with Eq. (4). More significantly, it agrees with the observation of Wang and Perdew[2] that the RPA correlation hole in the low-density limit screens out the exchange hole on the scale of $r_s a_0$, with additional structure on the smaller scale of $r_s^{3/4} a_0$. Our new observation that the leading term of Eq. (2) is independent of particle statistics is consistent with the divergence of the Fermi wavelength $2\pi(4/9\pi)^{1/3} r_s a_0$ on the scale of $r_s^{3/4} a_0$ as $r_s \to \infty$.

Finally, we argue that the low-density limit of the RPA correlation energy, although universal, is spurious: The term $(-0.803\ \mathrm{Ry})\ r_s^{-3/4}$ arising from the ring diagrams must be cancelled exactly by a similar term from another class of diagrams. This observation may be useful for the construction or testing of proposed corrections to the RPA.

Lieb and Narnhofer[7] proved that the electrostatic energy (electron-electron plus electron-background plus background-background) of charged particles in a uniform neutralizing background is bounded from below. The electrostatic energy per particle is

$$\varepsilon_x + \varepsilon_c - t_c \geq (-1.80\ \mathrm{Ry}) r_s^{-1}\ , \tag{6}$$

where ε_x is the exchange energy and t_c is the positive correlation contribution to the kinetic energy. As a result, the exact (beyond the RPA) correlation energy is also bounded:

$$\varepsilon_c \geq (-1.80\ \mathrm{Ry}) r_s^{-1} - \varepsilon_x\ , \tag{7}$$

where $-\varepsilon_x = d_1^{\rm RPA}(\zeta) r_s^{-1}$ for fermions. [The bound of Eq. (7) is very close for electrons in the low-density limit, as demonstrated by results for the Wigner crystal and from the Green's-function Monte Carlo results of Ceperley and Alder.[4,8,9]] Thus the RPA limit $(-0.803 \text{ Ry}) r_s^{-3/4}$ for $r_s \to \infty$ must be cancelled by corrections to the RPA. Since the Lieb-Narnhofer bound is independent of particle spin and statistics, this cancellation must also be universal.

An example of the exact cancellation of the RPA is known for finite temperature T in the classical limit ($\hbar \to 0$). In this limit, the RPA gives the Debye-Hückel plasma energy $\varepsilon_{\rm RPA}$:

$$\varepsilon_{\rm RPA}/kT = -1/(12\pi n \lambda_D^3) = -\Gamma^{3/2}/\sqrt{3} \; , \tag{8}$$

where $\lambda_D = [kT/(4\pi n e^2)]^{1/2}$ is the Debye length and $\Gamma = e^2/(r_s a_0 kT)$ is the strong-coupling plasma parameter. The RPA energy is rigorous and exact as $\Gamma \to 0$ but is quite wrong as $\Gamma \to \infty$. The Abé nodal expansion[10] gives corrections to the Debye result in the form of cluster integrals involving the Debye screened potential, $(e^2/r)\exp(-r/\lambda_D)$. It has been shown that, in the large-Γ limit, each piece of the Abé expansion begins with a term of order $\Gamma^{3/2}$, and summation to infinity of these terms exactly cancels the Debye-Hückel energy.[11] The remainder after this cancellation is of order Γ. The hypernetted-chain equation (HNC) for the Coulomb potential also accomplishes this cancellation, and in the large-Γ limit gives $\varepsilon/kT = -(9/10)\Gamma$, the Lieb-Narnhofer lower bound, for the energy of the classical strongly coupled Coulomb fluid.[12] It is probable that the quantum form of the Abé nodal expansion would also cancel the $T=0$ quantum RPA result in the strong-coupling limit as in the classical case, but this cancellation has not yet been explicitly demonstrated.

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[1]M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).
[2]Y. Wang and J. P. Perdew, Phys. Rev. B **44**, 13 298 (1991).
[3]S. Mizawa, Phys. Rev. **140**, A 1645 (1965).
[4]J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[5]H. E. DeWitt, J. Math. Phys. **3**, 1216 (1962).
[6]L. L. Foldy, Phys. Rev. **124**, 649 (1961).
[7]E. H. Lieb and H. Narnhofer, J. Stat. Phys. **12**, 291 (1975); **14**, 465 (1976).
[8]D. Ceperley, Phys. Rev. B **18**, 3126 (1978).
[9]D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[10]R. Abé, Prog. Theor. Phys. **22**, 213 (1959).
[11]S. G. Brush, H. E. DeWitt, and J. G. Trulio, Nucl. Fusion **3**, 5 (1963).
[12]K. C. Ng, J. Chem. Phys. **61**, 2680 (1974).